ASYMMETRIC DIELS-ALDER REACTION OF *tert*-BUTYL 2*H*-AZIRINE-3-CARBOXYLATE BY A SELF-ASSEMBLED COMPLEX OF BINOL, Mg AND Zn

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In the past the reaction of *tert*-butyl 2*H*-azirine-3-carboxylate (1) with 1,3-butadienes containing a glucosyl moiety as chiral auxiliary showed complete facial selectivity.^[1] However, the reaction of erythrose diene 2 with the same azirine 1 proceeds with low selectivity giving a 2.5:1 mixture of compounds 3 and 4.

In an attempt to overcome this lack of selectivity the reaction components were tethered in a LACASA-Diels-Alder cycloaddition (LACASA-DA) using a bimetallic complex of Mg(II) and Zn(II) having R-/S-BINOL as chiral ligand. This method had been first developed by Inomata in reaction of dienol with nitroso dienophiles, in the presence of tartaric acid-zinc complex.^[2] Later Ward reported a highly enantioselective LACASA-DA reaction of diene **5** with methyl acrylate.^[3]



Bearing in mind the result obtained by Ward, we combined the same diene (5) with azirine 1. The reaction proceeded at low temperature giving homochiral compound 6 in two diastereomeric forms depending on the stereochemistry of BINOL chiral inductor (R/S). Application of this methodology to reaction of chiral diene 2 with azirine 1 also gave complete facial control affording products 3 or 4 according to the BINOL chiral ligand. Non-optimized yields of products ranged from 30-50 %.

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- ^[2] a) Ding, X.; Ukaji, Y.; Fujinami, S.; Inomata, K. *Chem. Lett.*, **2003**, 32, 582-583. b) Ukaji, Y.; Inomata, K. *Synlett*, **2003**, 1075-1087.
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